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14. ABSTRACT A NETZSCH DSC 404F3 Pegasus® thermal analysis equipment has been acquired for monitoring effects of physical, mechanical and chemical changes, introduced in materials due to shock compression and high-strain-rate deformations. It includes two furnaces, a rhodium furnace capable of measurements of specific heat at temperatures up to 1650oC and a SiC furnace for analysis up to 1550oC under normal atmosphere, and static and dynamic inert gas atmosphere. The system uses the Proteus measurement and analysis software for data acquisition, storage and evaluation with MS WINDOWS platform, which enables multitasking with simultaneous evaluation and operation.					
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Report Title

Final Report: Thermal Analysis for Monitoring Effects of Shock-Induced Physical, Mechanical, and Chemical Changes in Materials

ABSTRACT

A NETZSCH DSC 404F3 Pegasus® thermal analysis equipment has been acquired for monitoring effects of physical, mechanical and chemical changes, introduced in materials due to shock compression and high-strain-rate deformations. It includes two furnaces, a rhodium furnace capable of measurements of specific heat at temperatures up to 1650oC and a SiC furnace for analysis up to 1550oC under normal atmosphere, and static and dynamic inert gas atmosphere. The system uses the Proteus measurement and analysis software for data acquisition, storage and evaluation with MS WINDOWS platform, which enables multitasking with simultaneous evaluation and operation of several thermal analysis approaches. The acquired system is being employed for understanding of polymorphous and amorphous-to-crystalline phase transformations, as well as non-homogeneous deformation occurring via shear banding in metallic glasses. The instrumentation will also be of benefit to our other DoD supported work on understanding of shock-activation leading to reactions in energetic/reactive materials. The thermal diagnostics equipment extends our current instrumentation capability beyond time- resolved measurements of shock stress and particle velocity measurements performed with gas-gun and laser-flyer impact experiments by providing a reference based on pre- and post-analysis for evaluating the effects of shock compression of inert and reactive materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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TOTAL:

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(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Manuscripts:

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Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

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FTE Equivalent:	
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Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Alex Bryant	0.00	
Rene Diaz	0.00	
Jennifer Breidenich	0.00	
FTE Equivalent:	0.00	
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<u>NAME</u>
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Names of personnel receiving PHDs

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Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Project Title: Thermal Analysis for Monitoring Effects of Shock-Induced Physical, Mechanical, and Chemical Changes in Materials

Contract No.: W911NF-13-1-0295

Abstract

A NETZSCH DSC 404F3 Pegasus® thermal analysis equipment has been acquired for monitoring effects of physical, mechanical and chemical changes, introduced in materials due to shock compression and high-strain-rate deformations. It includes two furnaces, a rhodium furnace capable of measurements of specific heat at temperatures up to 1650°C and a SiC furnace for analysis up to 1550°C under normal atmosphere, and static and dynamic inert gas atmosphere. The system uses the Proteus measurement and analysis software for data acquisition, storage and evaluation with MS WINDOWS platform, which enables multitasking with simultaneous evaluation and operation of several thermal analysis approaches. The acquired system is being employed for understanding of polymorphous and amorphous-to-crystalline phase transformations, as well as non-homogeneous deformation occurring via shear banding in metallic glasses. The instrumentation will also be of benefit to our other DoD supported work on understanding of shock-activation leading to reactions in energetic/reactive materials. The thermal diagnostics equipment extends our current instrumentation capability beyond time-resolved measurements of shock stress and particle velocity measurements performed with gas-gun and laser-flyer impact experiments by providing a reference based on pre- and post-analysis for evaluating the effects of shock compression of inert and reactive materials. It also enables us to determine if the distinguishing aspects of shock-compression are dominated by thermodynamic or kinetic effects, and thereby permit design of materials based on their exploitation for desired performance and application. The capability is also important for the research and education of our students, who are being trained with use of various time-resolved and post-mortem measurements and computations for developing and validating models, relevant to materials design, so that they are prepared to work in defense and national security work-force.

Problem Statement Being Addressed

Shock-compression response of metallic glasses: The response of metallic glasses under conditions of extreme pressure and strain rate is being investigated using laser-generated shock-compression and quasi-isentropic (shock-less, ramped-compression) experiments performed at the OMEGA lasers in collaboration with LLNL. One of the issues being investigated under these extreme conditions is how viscosity differences between the alloy-melts and frozen-liquid states (metallic glass) contribute to mechanisms of homogeneous and/or inhomogeneous flow characteristics. While crystalline solids can transform to highly disordered and amorphous states under high-pressure, the transformation response of metallic glasses under competing effects of large kinetic barrier and thermodynamic stability is another aspect that needs to be determined. Recent studies¹ employing static high pressure work at the APS have shown that Ce₇₅Al₂₅ metallic glass undergoes transformation from the amorphous state at ambient conditions to FCC crystalline state at 25 GPa. Ce₇₅Al₂₅ is an interesting metallic glass as it possibly contains a

random mixture of the elements. Pure Ce and Al have an fcc structure and upon solidification often produce preferred orientation. At ambient pressure, Ce has an atomic volume twice that of Al, but a lower electronegativity. Because of this extreme mismatch between the two atoms, solidification of the alloy from the melt results in the formation of a glass, which however shares the common long-range topological relationship with the fcc crystal, albeit without its long-range spatial periodicity, consistent with the cluster packing model typical of glasses. Upon being compressed, the atomic volume of Ce collapses due to the delocalization of the 4f electrons, which reduces the differences between the compressed Ce and Al and results in the Hume-Rothery criteria for crystallization of fcc solid solution. Pressure-induced devitrification then restores the hidden long-range through the transformation into a single crystal.

The question raised from the results of this study employing static high pressures, is the potential effect of dynamic application of high pressure, both in the context of the thermodynamic influence associated with the stress state (hydrostatic versus deviatoric) and the kinetic influence due to the duration of pressure application. Our current research addresses these key fundamental issues, namely, the influence of the thermodynamic and kinetic effects and the differences in material response between micro-crystalline, nano-crystalline, and amorphous solids at very high pressures and strain rates. Laser-shock studies at extreme conditions fill a critical void in experimental studies on metallic glasses for which there exists no equivalent work at extreme pressure and strain-rate conditions. Use of the high-energy laser facilities also allow us to employ advanced, time-resolved x-ray diagnostics, such as x-ray Thomson scattering, EXAFS, and dynamic x-ray diffraction. Furthermore, the exquisite control of the loading, including shock versus shock-less ramped-compression, require the shaped pulse control available only with these laser compression approaches. Techniques previously established by Remington et al² for shock and quasi-isentropic ramped pressure loading at NIF are being employed. Velocity interferometry (VISAR) measurements are performed to record the wave profile, and determine the shock compressibility and associated changes due to phase transitions. Time-resolved x-ray Thomson scattering, EXAFS, and dynamic x-ray diffraction studies are being attempted to probe the local lattice order for inferring changes in compressibility due to phase change, and temperature increase associated with localized inhomogeneous strain.

Thermal Property Measurements using DSC/DTA: Differential scanning calorimetry (DSC) measures the heat release (by monitoring the difference in heat flow to the sample and a reference) associated with phase transitions and chemical reactions as a function of temperature. Since the DSC is at constant pressure, heat flow measured is equivalent to enthalpy changes:

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt}$$

Here, dH/dt is the heat flow measured in mcal/s. The heat flow difference between the sample and reference is:

$$\Delta \frac{dH}{dt} = \left(\frac{dH}{dt}\right)_{\text{sample}} - \left(\frac{dH}{dt}\right)_{\text{reference}}$$

The value of $\Delta(dH/dt)$ can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than to the

reference. Hence, $\Delta(dH/dt)$ is positive. In an exothermic process (i.e., crystallization, oxidation reactions, and some decomposition reactions), the opposite is true and $\Delta(dH/dt)$ is negative. While there are advantages to using DSC, due to the accuracy of measuring the specific heat, C_p , and the heat released, ΔH , the primary disadvantage is the limited temperature range ($<1000^\circ\text{C}$).

For combined DSC and DTA (Differential Thermal Analysis) systems, the DTA component allows for a much higher temperature range ($>2000^\circ\text{C}$ for some DSC/DTAs). Hence, temperature range allows for identification of thermal events associated the glass transition temperature (T_g), crystallization temperature (T_x), solidus temperature (T_s), and liquidus (or melt) temperature (T_L), as shown in Figure 1.

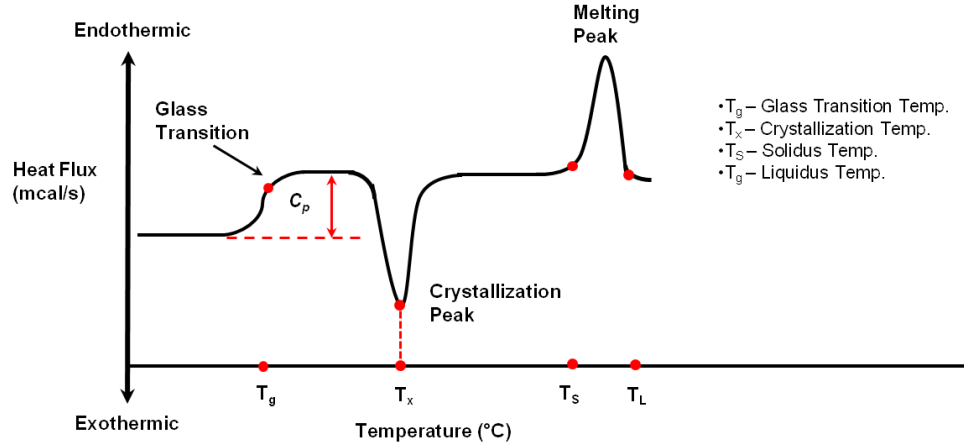


Fig. 1 – Typical DSC/DTA scan. Glass transitions cause a baseline shift which can be used to measure heat capacity. Crystallization is a typical exothermic process and melting a typical endothermic process. The ΔH associated with transformation is calculated from the peak area.

The transformation temperatures for metallic glasses allow determination of the criteria for glass-forming ability (GFA). The Turnbull Criterion for GFA is called the “Reduced Glass Transition Temperature” or T_{rg} ³, which is a ratio between the liquidus (T_L) and glass transition (T_g) temperature.

$$T_{rg} = \frac{T_g}{T_L}$$

Based on nucleation theory, Turnbull suggested that for an alloy having $T_{rg} \geq 2/3$, homogeneous nucleation of the crystalline phase is completely suppressed. The more advantageous use of the T_{rg} is in the effect of varied solute content. The argument towards forming metallic glasses at “deep eutectics” is employed by this relation since the liquidus temperature goes increasingly away from the glass transition temperature as function of solute content. Another criterion for GFA is the width of the supercooled liquid region or $\Delta T_x = T_x - T_g$ ⁴, in which large values of ΔT_x indicates high GFA and stable glass phases resisting crystallization⁴.

The effect of shock-compression on the phase transitions in metallic glasses has been studied using DSC⁵ analysis, which shows an increase in the temperatures of the primary thermal events, as seen in Figure 2. The differences correspond to overall change in glass formability of these samples^{i,iii}. XRD traces in Figure 3 reveal scans before and after shock compression of the same metallic glass, revealing the occurrence of precipitation upon shock-compression.

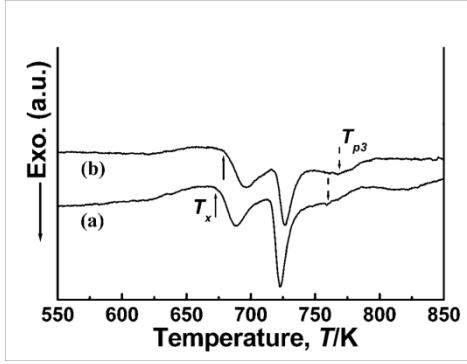


Fig. 2. DSC traces of BMG alloy at a heating rate of 10 K/min under a flow of purified argon a) as water-quenched and b) after shock impact at 45 GPa.

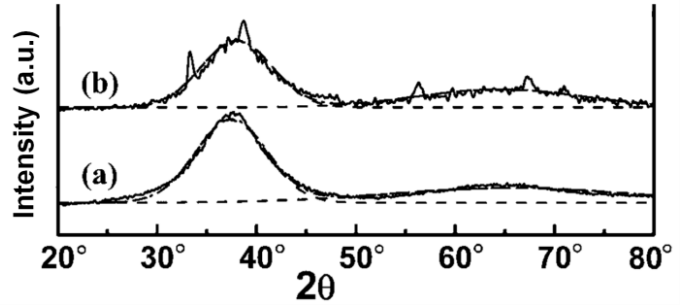


Fig. 3. XRD patterns of BMG alloy a) as water-quenched and b) after shock impact at 45 GPa. The overlaying dashed curves correspond to multi-peak fitting of the corresponding XRD patterns

The apparent activation energy determined from the DTA analysis performed at different heating rates and using the Kissinger method⁶ was observed to be higher for the shock-compressed metallic glass. Figure 4 shows the results for the shock loaded sample and Table I lists the differences in activation energies between the as-quenched sample (0 GPa) and the shock loaded sample (at 45 GPa). The increase in activation energy corresponds to an increase in the thermal stability of the glassy state. The results illustrate that activation the energy measurements allow for a better understanding of the growth kinetics of possible precipitation processes in the metallic glass. Combining DSC and XRD information, then makes it possible to obtain full information about transformation temperatures, the number of stages in which the transformation is occurring, details about the product(s) of each individual transformation (crystal structure, microstructure, and chemical composition), and the activation energy (and corresponding mechanism) for the transformation.

Table 1. The apparent activation energy of the glass transition (E_g), crystallization (E_x) and crystallization peak (E_{p1} and E_{p2}) calculated from Kissinger method for the BMG. Sample 0 and 45 are the as-quenched and partially crystallized, shock impacted samples.

Samples	E_g (kJ/mol)	E_x (kJ/mol)	E_{p1} (kJ/mol)	E_{p2} (kJ/mol)
Sample 0	281.7	132.0	130.7	208.6
Sample 45	312.9	151.5	181.3	271.7

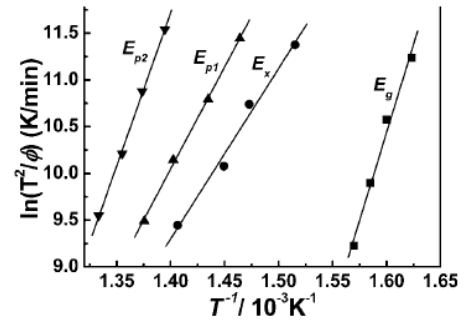


Fig. 4. Kissinger plots of E_g , E_x , E_{p1} , and E_{p2} for the partially crystallized BMG after shock impact at 45 GPa.

Components and Specification of Acquired Thermal Analysis Instrumentation

The thermal analysis instrumentation acquired in this project includes the NETZSCH 404F3 Pegasus® DSC (as shown in Figure 5) with two furnaces, a rhodium furnace capable of measurements of specific heat at temperatures up to 1650°C and a SiC furnace for analysis up to 1550°C under normal atmosphere, and static and dynamic inert gas atmosphere. The system includes the Proteus measurement and analysis software for data acquisition, storage, and evaluation using MS WINDOWS. The acquired system is being employed for understanding of polymorphous and amorphous-to-crystalline phase transformations, as well as non-homogeneous deformation occurring via shear banding in metallic glasses. The instrumentation will also be of benefit to our other DoD supported work on understanding of shock-activation leading to reactions in energetic/reactive materials.

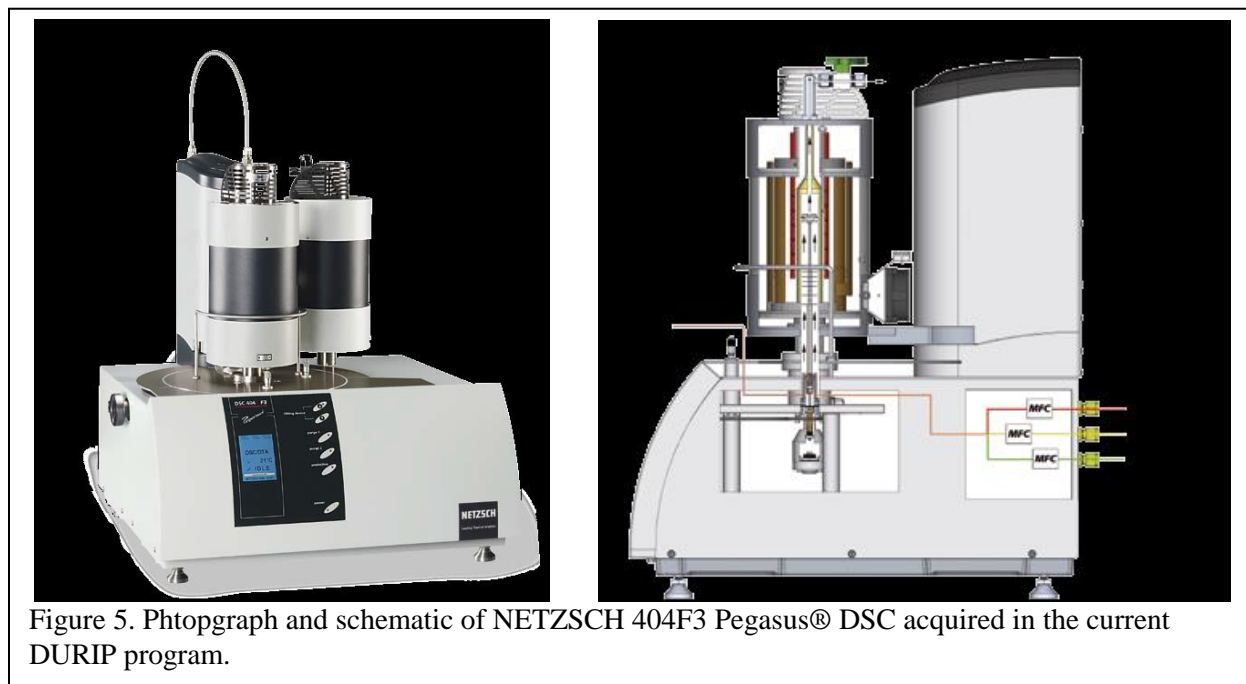


Figure 5. Photograph and schematic of NETZSCH 404F3 Pegasus® DSC acquired in the current DURIP program.

The thermal diagnostics equipment extends our current instrumentation capability beyond time-resolved measurements of shock stress and particle velocity measurements performed with gas-gun and laser-flyer impact experiments by providing a reference based on pre- and post-analysis for evaluating the effects of shock compression of inert and reactive materials. It also enables us to determine if the distinguishing aspects of shock-compression are dominated by thermodynamic or kinetic effects, and thereby permit design of materials based on their exploitation for desired performance and application. The capability is also important for the research and education of our students, who are being trained with use of various time-resolved and post-mortem measurements and computations for developing and validating models, relevant to materials design, so that they are prepared to work in defense and national security work-force.

The main components and specification of the acquired thermal analysis system are:

- NETZSCH 404F3 Pegasus® DSC with sample carrier support that provides reproducible adjustment, built-in μV -preamplifier electronics, furnace control, power supply and electric motor driven furnace hoist as the basic system. It has three magnetic valves and gas frits for purge gas inlet to the sample, and it is suitable for measurements under normal, dynamic, and static inert gas atmosphere. The Proteus measurement and analysis software for the DSC 404 F3 is used for data acquisition, storage and evaluation using MS WINDOWS, enabling multitasking with simultaneous evaluation and operation of the DSC and DTA.
- The system includes two furnaces including an accessory kit for furnace hoist, with manual pivoting mechanism. The Rhodium high-temperature tube furnace has a temperature range of 25- 1650°C and is equipped with Rh meander heater, integrated protective tube for gas flow with stop valve and gastight heating chamber for protective gas operation of the heater. It contains an air-cooled double shell, integrated control type S thermocouple, and voltage supply (45 V max). The Silicon Carbide furnace has a working temperature range of 25-1550°C, and contains a high-temperature tube furnace with SiC heating element, integrated exchangeable protective tube for gas flow with stop valve, air-cooled double shell, integrated control type S thermocouple, and voltage supply with 75 V max.
- The DSC sample carrier system also used for specific heat determinations is complete with radiation shield and thermocouples type-S, two sample crucibles (PtRh) with lids for temperature range of 25-1500°C, and two other sample pans (Al_2O_3) with lids for range of 25-1650°C.
- The computer system includes a Core i5 processor, 3.10 GHz, 4 GB RAM, 500 GB hard disk, DVD + RW drive, Widescreen 22" Ultra VGA LCD monitor, Windows 7 Professional with 32 bit serial, USB, Ethernet Interfaces. The Proteus basic software runs with MS Windows. It includes TauR (trademark) software extension for determination of the influence of instrument time constant (Tau) and thermal resistance (R) in DSC signals, including the calibration with pure (metallic) standards and the subsequent deconvolution of the Tau and R influence within DSC data curves. The resulting DSC curve shapes represent the de-smeared true heat flow originating from the thermal and chemical processes of the sample, thereby having the influence of the instrumental setup be practically completely eliminated. The software extension for specific heat (C_p) determination, for data acquisition, storage and evaluation includes (a) features for calculation and graphic representation of C_p , temperature-dependent ability to add additional measuring curves, C_p curve comparison; (b) tabulated printout or ASCII file export of the calculated values, along with the DSC raw data; (c) possibility of automatic determination of the sensor head sensitivity through evaluation of calibration measurements; (d) determination of single values of the C_p curve or DSC curves; and (e) input routine for free definition of the C_p standard value tables. The software extension (BeFlat®) is available for correction of temperature and heating rate dependent DSC baseline deviations over a multidimensional polynomial function to achieve the highest baseline stability with minimal curve in wide temperature ranges.
- Calibration sample kit with 8 substances (400 mg each) for DSC/DTA calibration of enthalpy and temperature, and various additional sets of standard samples for calibration measurements for C_p or sensitivity and enthalpy.

Research Performed with Acquired Instrumentation

The acquired thermal analysis instrumentation includes capabilities to identify shock-induced physical, mechanical and chemical changes, using pre- and post-mortem thermal analysis. It is being used to study the polymorphous and amorphous-to-crystalline phase transformations, as well as effects of non-homogeneous deformation occurring via shear banding in metallic glasses. Pre- and post-mortem thermal analysis combined with time-resolved thermal diagnostics available in our lab is used to delineate the differences between the thermal and mechanical stability of metallic glasses, and establish the mechanisms of stress-induced phase transformations in comparison to thermally-induced phase changes.

Shock-induced phase changes in metallic glasses: Metallic glasses have been a subject of much interest due to their unique mechanical properties such as superior strength, large ductility in bending, high hardness, low coefficient of friction, high corrosion, oxidation and wear resistance, and excellent magnetic properties.⁷ However, the desirable properties of metallic glasses are accompanied by their inability to undergo homogeneous plastic deformation due to the absence of dislocation-mediated crystallographic slip. Metallic glasses are known to deform by shear banding, a particular mode of deformation of interest for certain applications, but which also causes them to be quite brittle and fail catastrophically due to uninhibited propagation of the bands. Understanding of the deformation and failure processes has given insight that the metallic glass structure can be tailored to control shear band propagation through intrinsically formed or extrinsically added crystalline phases. Presence of these phases causes nucleation of multiple shear bands and significantly increases the plastic strain to failure, as well as limits catastrophic failure.⁸ Strengthening and toughening of glasses has also been investigated through composite structures, with partial crystallization (devitrification) or via extrinsic additions of crystalline phases. In-situ formation of crystallites or condensed amorphous phases can limit shear transition zones (carriers of plastic flow) or render them immobile, thereby raising the strength. Likewise energy dissipated in causing the transformation, as well as transformed phases acting as barriers (of critical length scale or spacing) to propagation of catastrophic shear bands, can result in increased toughening. Dynamic high-pressure equation of state measurements on bulk metallic glasses have revealed evidence of transition to a high-pressure phase, but the structural characteristics of the high-pressure phase have not been fully characterized.⁹ While the evidence¹ of phase change is obvious based on the discontinuity observed in the pressure versus volume and shock versus particle velocity trends, the structural characteristics of the high-pressure phase structure remain to be determined. The presence of multiple components in Vitrealloy 106, made it difficult to estimate the properties of high-pressure states of all combinations of binary/ternary phase-separated compounds. The bulk modulus and density values obtained from the compressibility measurements did not correlate with high pressure states of any known Zr-based crystalline alloys, which led to the conclusion that the observed phase transition is a shock-induced poly-amorphism transformation. Hence, it is important to establish the transformation response in a binary/ternary metallic glass, so that the measured high-pressure state properties can be correlated with those of the crystalline states, thereby allowing clear delineation between crystallization and poly-amorphism transitions. Our work has continued on investigating metallic glasses based on binary Ni-P and Ce-Al metallic glasses, and the more complex Ti-based DV1 metallic glass alloy to identify the structural characteristics of the high pressure phase(s) formed, including the degree and uniformity of long- and short-range order.

Shock-Compression Experimental Methods and Diagnostics Employed: Investigation of dynamic pressure-induced phase transformations is being performed using shock-delivery systems, including our 80-mm and 7.63-mm gas-guns and the newly developed laser-accelerated mini-flyer impact set-up. With the combination of impact capabilities (described below), use of nano-second resolution stress, velocity, and imaging diagnostics, in addition to the thermal diagnostics instrumentation, we are able to subject materials to pressures of up to 60 GPa and nano-to-micro-second shock-pulse duration, to investigate the influence of stress/strain-states and strain-rates on transformation and strengthening/toughening response of metallic glasses over a wide range of impact conditions. *Plate-Impact Uniaxial Strain Experiments* are performed with our 80-mm single-stage gas gun to investigate the effects of stress state (normal and shear) and strain rates ($10^4 - 10^6 \text{ s}^{-1}$) on the mechanisms and kinetics of pressure-induced phase transformations. The experiments can be conducted under planar-parallel and inclined-plate impact conditions to study the synergistic effects of normal and shear stresses on shock-induced phase transitions in the binary and ternary bulk metallic glass samples. The peak pressure and duration of the shock pulse is varied by altering the impact velocity and the thickness of the flyer plate mounted on the projectile sabot, to investigate the thermodynamic and kinetic effects on the transformation mechanisms and competition between crystallization and poly-amorphism. The planar parallel plate-impact experiment is used to impact a flyer onto a driver plate to produce a well-defined shock pulse that propagates un-attenuated through the metallic glass sample sandwiched between two PVDF stress gauges, and employing the VISAR to monitor the back-surface sample velocity profile. *Uniaxial Stress Anvil-on-rod or Rod-on-Anvil Impact Experiments* are performed using the 80-mm and/or 7.62-mm gas gun to determine the intermediate strain rate (10^3 - 10^4 s^{-1}) yield and fracture strengths of the metallic glasses, to establish the effects of phase transformation on strain-rate sensitivity. The experiments involve use of VISAR (or PDV) interferometry to measure the velocity of the back (free) surface of the impacted rod-shaped sample in the case of the anvil-on-rod impact set-up. With the rod-on-anvil configuration, a transparent (sapphire) anvil surrounded by steel ring can also be used, and the velocity profile of the impact face can be measured. Real-time monitoring of transient deformation states using high-speed digital imaging is also performed with anvil-on-rod or rod-on-rod impact experiments to develop and validate constitutive relationships over a wide range of loading environments. The IMACON camera acquired with prior ARO-DURIP grant is used to capture 16 frames at 200 million frames per second or 50 ns inter-frame times. The transient deformation states captured by camera along with the final recovered impacted samples are correlated with predictions of numerical simulations to allow development and validation of models describing the mechanical and transformation behavior of metallic glasses. *Laser-accelerated Flyer-Impact* system is used to perform impact experiments on metallic glass ribbons. The system consists of a Continuum Powerlite Nd-YAG pump laser (3 J), Faraday isolator, Beam Shaper/Aperture and the experiment chamber. A 8-mm diameter top-hat laser beam transmitted through the various optics, is incident on the flyer plate assembly (metal foil mounted on glass substrate coated with 0.5 μm C, 0.5 μm , and 1.5 μm Al) and generates a plasma, launching the metal foil (e.g., Al, Cu, or Ta) of $\sim 3\text{mm}$ diameter and 25-50 μm thickness, at velocities up to 2 km/s to impact the target. A combination of VISAR and PDV interferometers are employed to obtain simultaneous velocity traces with both diagnostics, thereby allowing detailed information with nanosecond resolution (with VISAR), as well as the effects of velocity distributions (with PDV). *Direct Laser Shock Experiments using the OMEGA laser* are also being performed in collaboration with LLNL researchers to allow exquisite control of the loading process, including shock versus shock-less

ramped-compression, through shaped pulse control which is available only with these laser-compression approaches. Velocity interferometry (VISAR) measurements are used to record the wave profile, and determine the shock compressibility and associated changes due to phase transitions. Time-resolved x-ray Thomson scattering, EXAFS, and dynamic x-ray diffraction studies can also be performed to probe the local lattice order for inferring changes in compressibility due to phase change, and temperature increase associated with localized inhomogeneous strain.

Incorporation of Thermal Analysis with Shock Compression Experiments: Thermal changes can cause devitrification and crystallization of metallic glasses. Indeed this is what is used to determine the glass transition and crystallization temperatures in the DSC. However, pressure is another primary factor of interest on the crystallinity/amorphous state. Pressure has also been shown to induce amorphization of crystalline phases,¹⁰ long-range order of amorphous phases or polyamorphic first-order phase transitions characterized by abrupt density changes.¹¹ The localized stress of shear bands in BMGs can also induce crystallization.¹² Dynamic deformation associated with high-pressure shock compression of metallic glasses is expected to introduce phase changes, albeit under different thermodynamic and kinetic conditions, compared to those observed under static high pressure application. The predominance of shear provides a thermodynamic influence, while the short duration of the pressure pulse influences the kinetics of the transformation. Pre- and post-mortem thermal analysis is performed on BMG samples, to determine the degree of activation caused by shock compression, based on measurements of the heat flow conditions. With pre- and post-mortem thermal analysis performed using different heating rates, the apparent activation energy, determined using the Kissinger method, can be compared. For both homogeneous and heterogeneous nucleation, crystallization is normally resisted due to the increased activation barrier or facilitated due to creation of nucleation sites at defects generated due to shock compression. DSC measurements allow for the elucidation of changes in glass forming ability that occur with the different shock loading conditions. This information further helps to reveal the changes in metastability of the glass phases.

The Ce-Al binary metallic glass is a particularly interesting system, since it has been shown to crystallize to a single crystal fcc phase at static pressures exceeding 25 GPa. With Ce and Al, both having an fcc structure, pressure-induced formation of an fcc single crystal may be associated with the presence of ordered clusters of Ce and Al. Formation of single crystal under dynamic loading may not be favored due to crystallization being dominated by nucleation rather than growth processes during shock compression. Instead, dynamic crystallization to a polycrystalline compound may be expected beyond a certain applied shock pressure. It is however, important to follow the evolution of the crystallization process by simultaneously conducting XRD and DTA/DSC analysis on samples shock-compressed at pressures below the threshold to not only allow identification of phases formed via XRD analysis, but also the transformation temperatures and corresponding apparent activation energies based on DTA/DSC. In the present work, Ce₇₅Al₂₅ metallic glass ribbons made via melt spinning were obtained from Ames Laboratory. The as-received ribbons of 40 μm thickness had opposite surfaces with a matte and reflective finishes, with the matte finish corresponding to the surface in contact with the melt spinning wheel, and the reflective surface exposed to the environment. XRD analysis of the respective surfaces confirmed (as shown in Figure 6), that the reflective side had a partially crystalline oxide surface coating, closely matching with Ce₆O₁₁, and the matte side, however,

was clearly amorphous. The matte side surface corresponds to the melt being solidified in contact with the water-cooled copper wheel, resulting in the fastest cooling rate ensuring the amorphous state and replicating the surface texture of the copper wheel on the ribbon. The reflective side, exposed to the environment, albeit vacuum, has an oxide coating due to reaction with the trace amounts of oxygen present and partial crystallization due to somewhat slower solidification rate.

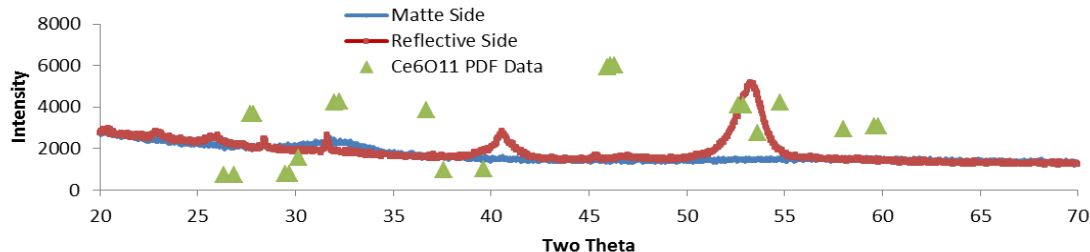


Figure 6. XRD results for the two sides of the melt-spun ribbons. The matte side is clearly amorphous while the reflective side has a crystallinity that matches the peaks for CeO.

Density measurements performed with the Archimedes method, employing a surface tension lowering liquid added to water and using a long ribbon piece, yielded a value of 5.93 g/cm^3 for the $\text{Ce}_{75}\text{Al}_{25}$ metallic glass ribbon, which is lower than the calculated density (6.21 g/cm^3) for the crystalline alloy obtained using the rule of mixtures. The metallic glass ribbons were also characterized via Local Electrode Atom Probe (LEAP) at ORNL. The results reveal that the metallic glass ribbons contain clusters of 80 atomic% Ce throughout the as-received sample. However, it was not obvious if these clusters are either nearly pure Ce or $\text{Ce}_{75}\text{Al}_{25}$. The DSC analysis performed using the NETZSCH 404 *F3 Pegasus* DSC is shown in Figure 7, which plots the heat released as a function of time and temperature, revealing the primary and possibly secondary crystallization events for the as-received $\text{Ce}_{75}\text{Al}_{25}$ metallic glass. Similar DSC curves for the

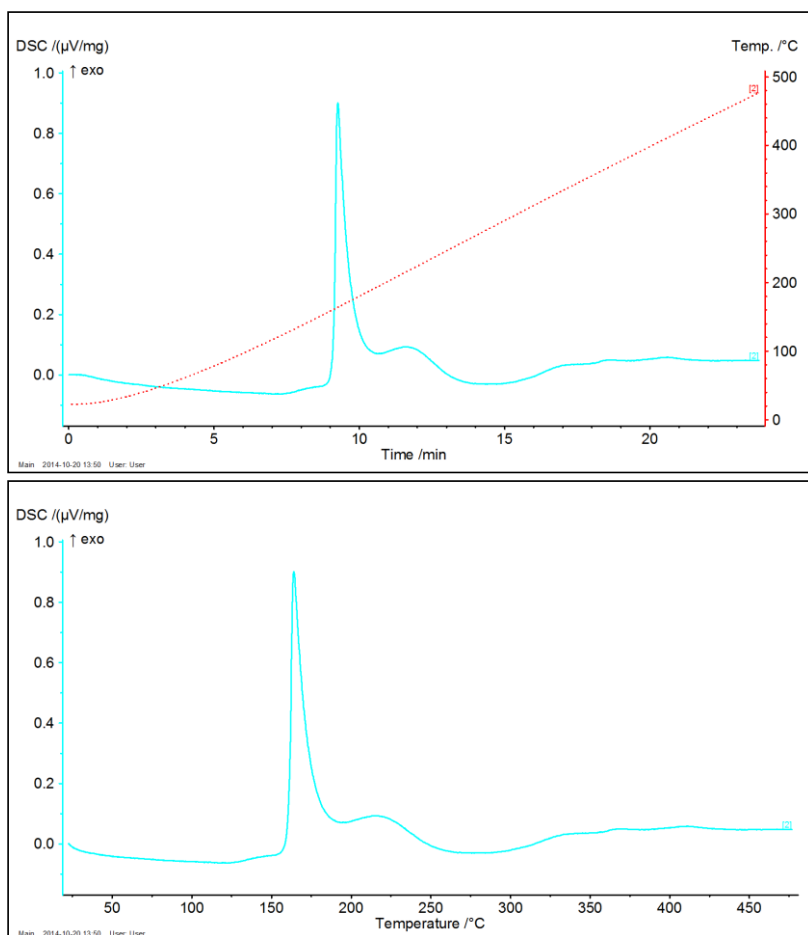


Figure 6. Plot showing heat released as a function of time and temperature, for the as-received $\text{Ce}_{75}\text{Al}_{25}$ metallic glass ribbon.

DV1 Ti-based bulk metallic glass sample are shown in Figure 7, revealing multiple crystallization and melting events in the as-received DV1 alloy, during the first heating cycle, and only the melting (of crystallized phases) event during the second heating cycle.

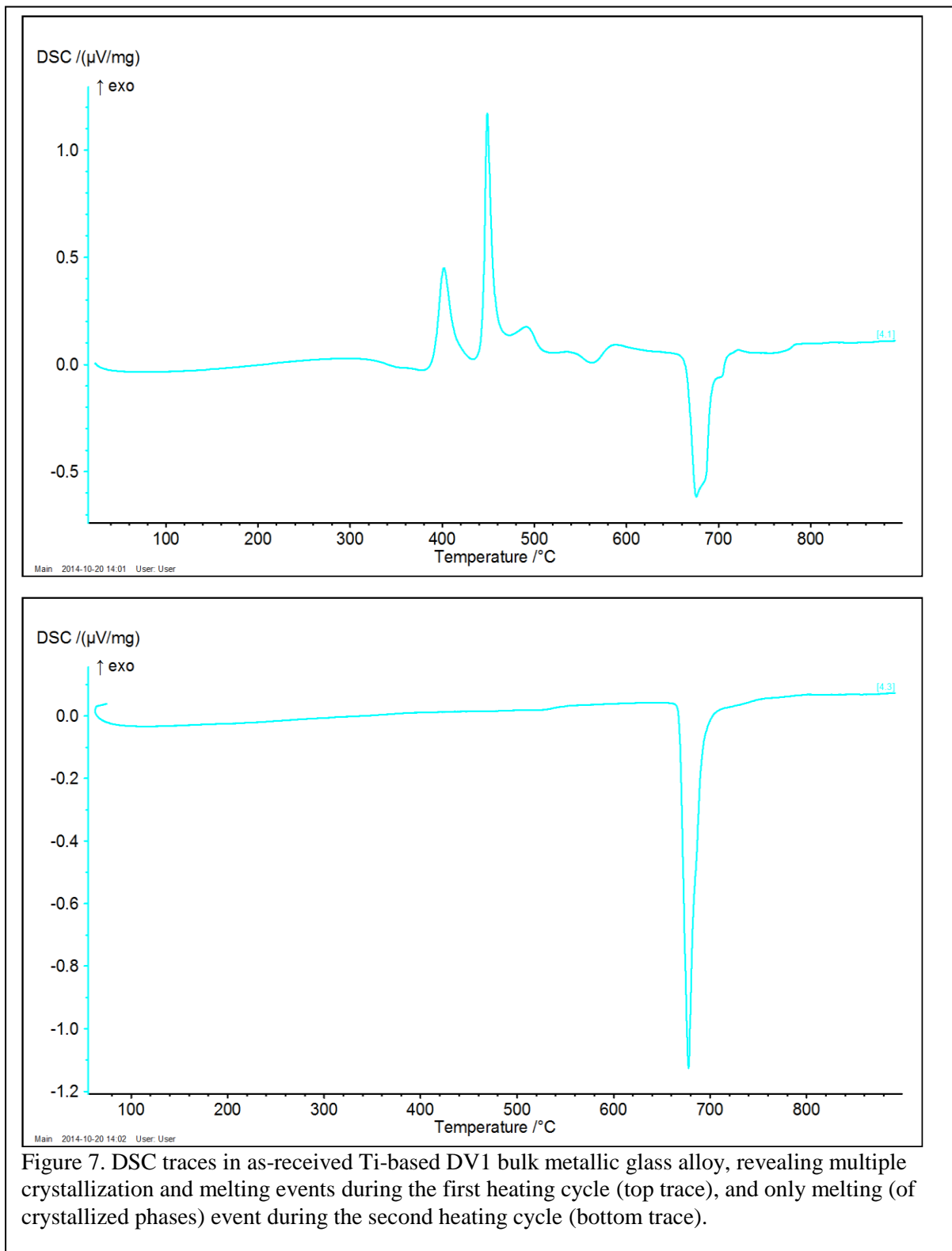


Figure 7. DSC traces in as-received Ti-based DV1 bulk metallic glass alloy, revealing multiple crystallization and melting events during the first heating cycle (top trace), and only melting (of crystallized phases) event during the second heating cycle (bottom trace).

Direct laser shock experiments have been performed the $\text{Ce}_{75}\text{Al}_{25}$ melt-spun ribbons, in collaboration with Bruce Remington and his group at the Lawrence Livermore National Laboratory, using the Omega and Janus laser facilities. The experiments were performed during two separate campaigns. In the first experiment, two 1mm x 1mm samples of $\text{Ce}_{75}\text{Al}_{25}$ melt-spun ribbons were placed into the laser sample recovery tubes at the Omega Laser Facility at the Laboratory for Laser Energetics (LLE) in Rochester, NY, and the shots were performed at 20J and 80J, respectively, in order to characterize the dynamic response at pressures slightly lower and higher than reported the 25 GPa hydrostatic pressure that resulted in instant and complete devitrification of $\text{Ce}_{75}\text{Al}_{25}$ in prior work. In the second experiment, four recovery tube-enclosed sample stacks of ~70 ribbons (each 1mm x 2mm x 40um) were shot at the Omega facility at 70J and 150J, with Hyades calculations showing large attenuation from the layers of the sample. Stacks were hit either into the face of the stack or into the edge of the stack so as to observe the different shock characteristics and characterize the different radial distribution of the shock energy effects in the two orientations. The edge on sample also ensured the laser would hit a relevant portion with less worry about errors in the adjustment. The recovered samples are being characterized using DSC/DTA, and XRD and TEM analysis.

Other DoD supported work on Advanced Reactive Materials

In other DoD/DTRA supported work, we are investigating the fundamental *spatial* and *temporal* understanding of the mechanisms of impact-initiated anaerobic chemical reactions in Al-based intermetallic reactive material systems. The overall objectives include, (a) determining the time sequence of processes/events associated with deformation and flow, fracture and fragmentation, and dispersion and mixing of reactants leading to initiation of anaerobic reactions, as well as subsequent interaction (combustion) with gases in environment; and (b) Establishing the role of material-inherent elastic/plastic properties and reactant configuration (e.g., porosity, morphology, distribution) on mechanisms and kinetics of meso-scale processes and resulting macro-scale energetic performance of anaerobic and combustion reactions. The understanding of critical characteristics of reaction processes requires establishing the complex stress-strain states as a function of the macroscopic material system geometry, impact configuration, and loading conditions, by probing processes (as shown in Figure 8) at the macro-scale of the bulk material, meso-scale representing certain volume element, micro-scale representing set of two or more particles, and nano-scale illustrative of an interface between particles. Also critical in this study is the delineation of the role of aluminum on its ability to undergo an aerobic (combustion) reaction versus anaerobic intermetallic reaction with other constituents. Consequently, the impact-initiated reactivity of Al by itself is being investigated which requires determining the thermal reactivity of Al following mechanical activation via various processes, through thermal analysis.

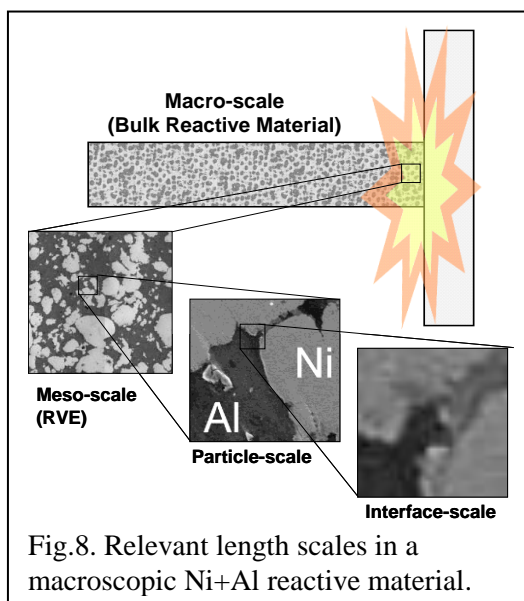


Fig.8. Relevant length scales in a macroscopic Ni+Al reactive material.

DSC Analysis of Retained Elastic Strain in Mechanically Pre-Activated Aluminum Powders:

DSC measurements were used to evaluate the bulk stored elastic strain energy in mechanically-activated aluminum powders. As temperature is increased during the DSC measurements, energy release due to stored elastic strain from presence of dislocations and point defects, on the material volume can be observed in the form of an exothermic peak. DSC measurements were performed on powder compacts that had been prepared by quasi-static pressing of mechanically pre-activated aluminum powders. The compacts were 3.2mm diameter by 1mm high and approximately 17mg in mass. Samples were loaded into a platinum-rhodium DSC pan with an alumina liner, and energy release information was collected on a Netzsch DSC 404F3 outfitted with a Rhodium furnace. The thermal program consisted of heating the sample to 50°C, holding at 50°C for five minutes, heating at a rate of 20°C/min to 375°C, followed by cooling back down to room temperature. Each temperature program was immediately followed by an identical program of that same sample to produce a baseline unique to that sample. The baseline measurement was subtracted from the initial measurement to produce the net heat flow curves, which are shown in Figure 9.

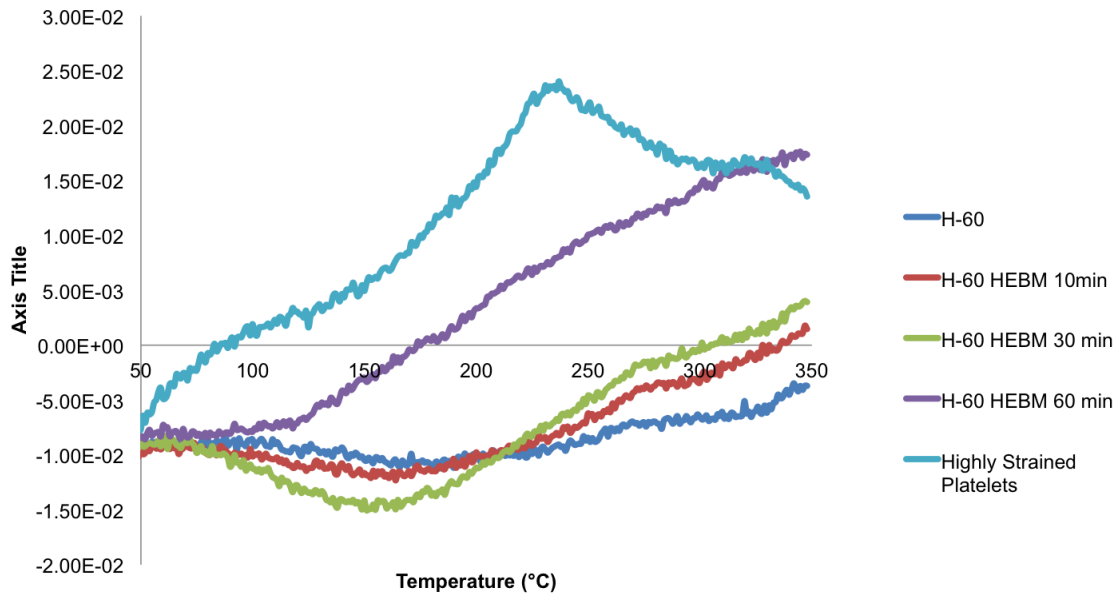


Figure 9. Heat flow curves from mechanically pre-activated aluminum powder compacts.

The DSC curves shown in Figure 9 indicate that the mechanically activated high-energy ball-milled (HEBM) aluminum powder samples contain almost no retained elastic strain energy. Alternatively, the peak at 231°C present in the highly strained aluminum platelet samples clearly indicates the presence of retained elastic strain energy in those samples.

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